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Ultrafast shape change and joining of small-volume materials using nanoscale electrical discharge

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ABSTRACT

Using nanoscale electrical discharge-induced rapid joule heating, we develop a method for ultrafast shape change and joining of small-volume materials. The shape change is dominated by surface tension-driven convection in the transient liquid melt, giving an extremely high strain rate ~10^6 s^{-1}. In addition, the heat in small volumes could be dissipated within a few microseconds through thermal conduction, quenching them back to the solid state with cooling rate up to ~10^8 K/s. We demonstrate this approach can be utilized for ultrafast welding of small-volume crystalline Mo (a refractory metal) and amorphous $Cu_{49}Zr_{51}$ without introducing obvious microstructure change, which is distinct from bulk welding.

1 Introduction

Driven by the miniaturization trend of devices, the mechanical properties of materials at the micro- and nano- scale have attracted intense interest worldwide [1-3]. It has been well-established experimentally that materials at this size regime exhibit extraordinary mechanical behavior compared with their bulk counterpart [4-8]. Take metallic glasses (MGs) as an example, it has been found that submicron sized MGs exhibit unique mechanical properties compared to

bulk samples, including unprecedented elastic strains (4 to 5%) [5, 9] and tensile ductility [7, 8, 10]. In addition, arrays and patterns of microscale MG structures can be formed by plastic molding in the supercooled liquid state above the glass transition temperature (T_g) [11, 12]. This suggests that submicron sized MGs can be excellent building blocks for small-scale architectures. However, in order to achieve intricate architectures, shape change and joining of individual components are usually necessary. For bulk glass work-pieces, effective routes are well known, such as blowing and molding in the liquid (or supercooled liquid) state [12, 13], and welding processes have been developed by many research groups in recent years [14, 15]. However for microscale MG components, the shaping and joining of individual component become a rather challenging issue. The processing challenge in the microscopic world arises from a number of unprecedented needs. First, one has to locate and manipulate a specific individual MG component, with sub-micrometer precision. Second, the heating has to be so fast and extremely focused (very small heat-affected zone), such that the component locally reaches high temperature to allow mass flow while other components and devices, which are only nanometers or micrometers away, are not affected. This requires intense but spatially and temporally very localized energy input. Third, rapid cooling of the heated (molten) sample is necessary to assure that the solidified product after reshaping/joining is a MG with completely amorphous structure, the same as the original (and other components in the system), without crystallization [4]. In the following we demonstrate a new nano-scale processing route that produces a sharp temperature spike very locally in the particular component of interest to reach all the above goals simultaneously. This novel method was inspired by spontaneous reshaping of micron-sized MG beams which we observed serendipitously, and later traced its origin to the ground potential fluctuation $V(t)$, which was not there by design.

2 Experimental

The schematic experimental design is displayed in Fig. 1A. A tungsten (W) tip and a conductive sample are connected to ground point G_1 and G_2, respectively, exhibiting a $V(t)$ as seen in Fig. 1B, measured by a voltmeter. Similar $V(t)$ are available in many other nano-manipulation and in situ observation systems, and for the purpose of reproducing the phenomena shown next such random energy reservoir can also be replaced by an alternative, more controlled electrical power source. The fact that there is a regular 50Hz component (Fig. 1B) means the external power supply contributes at least partly to the pumping of $V(t)$. On top of this regular component we also see a random fluctuation component that can run up to ±0.3 volt. Such fluctuating electrical energy supply can generate significant effect on small asperities prior to contact. This is because in an electromechanical system, there are effective capacitance C ($C \equiv Q/V$) as well as inductance L ($V \equiv LdI/dt$) distributed throughout, where C, L are geometry dependent. Such effective-circuit C and L may have dramatic impact on small asperities prior to contact because of electrical

discharge, since for example, $I=dQ/dt=CdV/dt$, and a relatively large current I may need to pass through very small asperities in a very short time to heat it to very high temperature. In Fig. 1A, R is an adjustable macro resistor introduced externally to impart controllability and R_1 is the systematic electrical resistance. W tip is driven by a Kleindiek Nanotechnik control system (connected with G_1), allowing movements in three directions (the finest step is 5 nm) plus a rotational degree of freedom. When the dimensions of the W tip and the sample are on the conventional length/size scales that we are normally accustomed to (e.g., millimeters and centimeters), the electrical field ($\boldsymbol{E}$) resulting from the minute potential difference is too small to generate any electrical discharging when they are driven toward to each other. However, the situation changes dramatically in the micro- and nano- world. The tungsten tip and sample in our design are now extremely "sharp tips", with their radius of curvature in the submicron range. It has been well known that a sharp tip could dramatically decrease the threshold voltage for field electron emission and discharge, such as in carbon nanotubes [16, 17]. When the tungsten tip is being brought towards sample, $V(t)$ will induce electrical charges with opposite signs on both side. As W tip is being brought close enough (e.g. tens of nm or less, depending on the $V(t)$) to the sample (connected to G_2), the tip-enhanced electrical field $\boldsymbol{E}$ goes up dramatically to reach a critical value for nanoscale electrical discharge (NED) due to the large local field enhancement factor of sharp geometry [18-22], even under very low voltage (Fig. 1B). Fig. 1C is a flowchart showing the time scales of the NED-induced pulse current, temperature evolution and shape change of the sample.

3 Results and discussion

We first show that NED can cause micron-sized Mo single crystal beams to undergo ultrafast and dramatic shape changes. In order to minimize the interim procedure as well as monitor the entire process, both the fabrication and tests of samples were conducted inside a Helios Nanolab Dura-beam focused ion (FIB). Electrical signal was simultaneously monitored using a Tektronix oscilloscope. Mo is a refractory metal with bulk melting temperature T_M=2896 K. Figure 2 shows the typical shape change of a Mo single crystal beam (See ESM and Fig. S1 for detailed sample preparation procedure). When the W tip was driven to approach the Mo beam (Fig. 2A), NED occurred suddenly and rendered the latter to separate and shrink into two parts with spherical ends (Fig. 2B). The estimated total volume after the dramatic shape change was almost the same as that of the initial beam, suggesting little mass loss due to evaporation. It is interesting to note that the W tip and the surrounding structure did not show detectable change during this process, as seen in Fig. 2B. The corresponding transient NED current (Fig. 2F) was recorded using an oscilloscope in parallel with a resistor (R=1 Ohm, see Fig. 1A). Note the electrical current lasted only ~ 1 microsecond. A second approach generated another NED, which made the beam rooted in its parent body into a "mushroom" geometry (Fig. 2C) in a very short time, as shown in Movie S1 in

ESM. In order to reveal its internal structure, the "mushroom" structure was thinned into a 100-nm-thick slice 1)red rectangular box) and examined inside a JEOL 2100F Transmission Electron Microscope (TEM). Surprisingly, the selected area diffraction pattern (Fig. 2D) and dark-field TEM observation (Fig. 2E) demonstrate that the "mushroom" interior is still single crystalline and has exactly the same lattice orientation as its parent body. This is quite different from traditional welding or laser melting processes, where the melt zone turns into a polycrystal. What occurred here seems to be rapid re-growth of the same crystalline orientation back into the liquid as it is quenched, since the liquid is still connected to the parent single crystal. The defects observed in Fig. 2E are attributed to gallium ion irradiation and implantation.

The observed phenomenon can be rationalized as below: based on the thermal and physical parameters of Mo [23], the transient input energy (~26 nJ) from Joule heating of the recorded electrical pulse in Fig. 2F would heat part of the Mo beam to the molten state; surface tension-driven mass transport will lead to the ultrafast shape change of Mo beam which will in turn break down the electrical connection, thus shutting off the NED energy feed, as seen in the flowchart of Fig. 1C. After that, the heat in Mo beam was dissipated through thermal conduction to the connected base material. The thermal diffusivity (α) of Mo is about 5.4×10^{-5} m^2/s at room temperature, and the characteristic time for temperature to decay obeys $\tau_T \sim L^2/\alpha$, where L is the thermal diffusion length in beams (~10 μm), so the time to cool down from T_M to room temperature is ~ 10^{-5} s, consistent with results of finite element modeling (Fig. S2 in ESM), giving a cooling rate ~10^8 K/s. This means the mass transport for shape change was terminated during this short time, with an extremely fast strain rate (~10^6 s^{-1}). The different morphologies (sphere-like versus mushroom) after two consecutive NEDs is attributed to the shortening of thermal diffusion distance, causing faster cooling in the latter case and the freeze-in of an unstable morphology. Very recently similar rapid heating and quenching route using electrical pulse has been successfully used for experimentally fabricating monatomic metallic glass at even smaller scale metals (tens of nanometer) with cooling rate as high as ~10^{13} Ks^{-1} [24]. While monoatomic metallic glass was fabricated at an extremely high cooling rate in Ref. [24], our application works at a relatively lower cooling rate, giving rise to the possibility of preserving original materials microstructure during welding. Besides, the ultrafast electrical pulse in our work can be induced by the nanoscale electrical discharge, taking the advantage of ground potential. This is very important because localized ultra-fast heating can be achieved on a wide range of sample shapes, instead of only sample regions where electrical resistance (heating) is promoted by geometry factors. [Compared with the difference structures in single element crystalline refractory metal, the quenched cooling rate in the ~40 nm length Ta crystal is larger than 10^{13} ks^{-1} and exceeds the critical cooling rate for vitrification of Ta atoms, while the cooling rate in this work for the Mo component at the microscale is pretty fast than that in macro scale but still much lower than the critical rate for Mo vitrification.]

Similar fast mass transfer was also observed for $Cu_{49}Zr_{51}$ MG beams, as shown in Fig. 3. Its glass transition temperature is of T_g ~700 K and liquidus temperature of T_l ~1200 K [25]. NED

occurred when W tip was driven to approach sample, the original beam shrunk into a sphere without breaking, as seen in Fig. 3B and Movie S2 in ESM. The observed sphere-like shape is indicative of the operation driven by surface tension. It is very interesting to note that the structure remained predominantly amorphous (Fig. 3C), except for a few isolated nanocrystals (~10 nm) on the surface. Apparently, due to the large heat sink the sample is attached to, the quench rate of the small molten beam (>10^7 K/s, in ESM) is fast enough to quench the liquid back into a glass. Such rapid cooling has also been reported during the formation of submicron-sized carbon glass beads, using an electrical arc method [26]. It is worth noting that the shape change and mass transport also depend on the sample size. Fig. 3D included a CuZr glass beam with larger size d. The shrinkage of the beam was stopped in the middle, in contrast to the smaller beam which shrunk into spheres in Fig. 3B. This is because that Joule heating-induced ΔT decrease dramatically as increasing sample size (~ d^{-4}, see ESM). At the same time, larger sized samples are expected to have better thermal conduction and faster cooling rate.

Comparing the morphologies in Fig. 2 and Fig. 3, the shrinkage of Mo beam was terminated in the middle with a mushroom shape while the CuZr sphere reached the base material. Thermodynamically, both the molten Mo and CuZr beams would be driven towards a sphere-like (low energy) shape by surface tension, but this mass transport would be kinetically affected by the surface tension, thermal diffusivity and the dimensions of the studied samples. The thermal diffusivity of CuZr glass is one order smaller than that of refractory Mo [27, 28] and the length of CuZr MG beam is similar to Mo beam, thus longer time to stay at high temperature than that of Mo beam (finite element analysis in Fig. S2) would contribute into greater mass transport and shape change to form a sphere. Besides the aforementioned factors, the outcome of the mass transport (morphology) also depends on the tunable resistor R_1, which could influence the discharge pulse intensity (See the details in ESM).

As the behaviors are seen to be generic, some analysis is in order. The observed phenomena involve coupled electrical, thermal (τ_T) and mass (τ_M) transport, with intrinsic characteristic timescales denoted in the brackets. A logic flowchart is shown in Fig. 1C. From Fig. 2E and 3E, we know that the NED persisted for $\tau_E \sim 10^{-6}$ s. Electrical discharge is a complex phenomenon [18-22]. Once NED starts, some atoms may evaporate from the solid surface and get ionized into plasma, which sustains the discharge, forming a nano- or micro-arc [21, 22], despite the two electrodes are not in physical contact. Eventually, as the tips recede far enough, NED would stop. Let us say that the beam has a characteristic length L, and the receding tip ("mushroom") has a characteristic radius of curvature r. Initially $r \propto d$, the diameter of the beam. As the beam is connected to a large heat sink, $\tau_T = L^2/\alpha$. For crystalline Mo, $\alpha \sim 5\times10^{-5}$ m^2/s, so for L=5μm, τ_T ~5×10^{-7}s. We thus see that τ_E and τ_T roughly match each other. Next we show that the intrinsic mass transport timescale τ_M could be much faster than τ_E, τ_T if convective flow occurs. If the "mushroom" region (e.g. Fig. 2C) with characteristic curvature r has fully melted, $T>T_M$, and the liquid has shear viscosity η_{liquid}, a liquid tip would recede under Young-Laplace pressure difference $\Delta P \sim \gamma/r$, with strain rate ~ $\Delta P/\eta_{liquid}$ and maximum receding velocity $v_{max} \sim r\cdot\Delta P/\eta_{liquid}$

~ γ/η_{liquid}. Taking γ = 2.08J/m^2, η_{liquid} = 5.6×10^{-3} Pa·s for liquid Mo at its melting point [23], we predict v_{max} ~ 400 m/s, which is length scale independent. This is verified by direct MD simulation of fully molten Mo mushroom which receded by 20nm in 84 ps, with v_{max} ~ 250 m/s (Fig. 4). Thus, *if* the mushroom is fully molten, the shape change timescale would be $\tau_M \sim r / v_{max}$. This suggests that even for a large mushroom, r = 1 micron, τ_M would still be 2-3 orders of magnitude smaller than τ_E, τ_T. This means that if convection is activated, the intrinsic shape change ability is so good that τ_M would not be the bottleneck. In this mass-transport scenario (scenario I), the shape change would be thermally limited, that is to say, the liquid portion would "instantaneously" take their minimum-capillary-energy configuration (with respect to the solid) seen at the timescale of τ_E, τ_T (τ_E, τ_T clearly control the phase change).

There is an alternative mass-transport scenario (scenario II), where we assume there is pre-melting of the surface [29, 30], but no bulk melting as the local temperature is not high enough, $T<T_M$. In this case, Coble creep [30] of the mushroom would occur, which is a surface-diffusion driven shape change without convection. However, a semi-quantitatively calculation (See ESM) indicated that the shape change capability of Coble creep would be 6 to 9 orders of magnitude less than the convective flow scenario I. By this reckoning then, the characteristic timescale τ_M would fall into the range of seconds. Indeed, we have recently observed Coble creep induced shape change in tin at T=0.6T_M with in situ TEM, at timescale of 0.1 s [30]. Scenario II, therefore, cannot explain the experimental results here, because (a) with $\tau_T << \tau_M$, surface diffusion would long have been "frozen out" as the temperature recovers to room temperature in Mo, and (b) with the recording time resolution of the in situ SEM movies, we should have recorded the shape change *process* if that timescale falls into the range of 0.1 s, as is the case with Sn, but we have not. For these reasons, scenario II is self-contradictory and can be excluded. We are left with scenario I, thermally limited capillary-driven convective flow, as the only possible scenario. The heating up, quenching down and shape change are thus all predicted to occur with characteristic timescale 10^{-6} s.

We next demonstrate that NED can be used for ultrafast mass transport and joining of small volume materials which is different from the micro- and nano- scale joining methods reported so far [31, 32]. In Fig. 5A, a piece of Mo single crystal adhered on the W tip was driven to approach the Mo base material. With NED occurring between the two ends, the induced mass transport at the interface results in joining of the two parts (Fig. 5B). After the joining, we pulled back the W tip to exert mechanical load on the entire structure. The beam eventually fractured at the right end (Fig. 5C), rather than at the welded regions (the W/Mo and Mo/Mo joints), indicating that the welded regions were not mechanically weaker than other parts of the beam. The welded region also produced no obvious Kapitsa (interfacial) electrical resistance. Thus the weld is mechanically and electrically sound.

A second example is shown in Fig. 5D through Fig. 5F, where three separated CuZr glass beams were designed and fabricated using FIB. Upon NED between the W tip and beam 1, mass transport was induced for beam 1 (as a sacrificial beam) to fill the gap between beam 2 and beam

3 (Movie S3 in ESM). FIB cutting revealed that the unification was perfect in the joint, as seen in the cross-sectional view in Fig. 5F.

4 Conclusions

The examples above highlight the advantages of the NED-induced welding. It is highly local; the heat affected zone is small, and the microstructure in the joint closely resembles the internal (crystalline or amorphous) structure of the rest of the components. It is also chemically clean, without the need for a solder, a flux or a braze layer. Through careful *in situ* electrical measurement, electron microscopy and modeling, we have determined that these morphological changes occur by thermally limited capillary-driven convective flow of liquid melt, rather than by surface-diffusion driven Coble creep [30] which would be substantially slower. The electrical discharge, heating up, quenching down and shape change should all occur within timescale of 10^{-6} s. The fact that one can use NED to make high-quality welds between high melting point metals (T_M(Mo)=2896 K, T_M(W)=3695 K) without affecting nanostructures nearby is technologically significant. Using NED to weld metal and semiconductor and between semiconductors are currently under way, and will be reported in another article.

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Figure Legends

Figure 1. The schematic of the design of NED and its working principle. (a) Schematic for the experimental set up. The tungsten tip and microscale sample are grounded at G_1 and G_2, respectively. The instantaneous electrical pulse is monitored by an oscilloscope (V meter) in parallel with a tunable electrical resistor, *R*. The black arrow indicates the moving direction of W tip. (b) The measured ground potential evolution of G_1 and G_2 in our lab. (c) A flow chart showing the time scale of the NED-induced pulsed current, temperature evolution and mass transport for shape change in micron-sized beams.

Figure 2. NED-induced ultrafast and dramatic shape change in single crystal Mo beam. (a) The W tip on the left was driven to approach the Mo beam with size of 520 nm ×480 nm ×10 μm. (b) The morphology of the Mo beam after the first NED process. (c) The beam continued to shrink and

formed a “mushroom” structure during the second NED, the inset showing a thinned mushroom structure. (d) and (e) are the selected area diffraction pattern and cross section view of the “mushroom” head, respectively. Both of them confirmed that the cap of Mo “mushroom” is same single crystal as its root. (f) Current evolution measured during the second NED.

Figure 3. NED-induced ultrafast and dramatic shape change in $Cu_{49}Zr_{51}$ MG beams. (a) The original morphology of the CuZr beam (1200nm ×700 nm ×9 μm). (b) After NED, the CuZr beam shrunk very fast to the right base, forming a hemisphere-like structure. The inset framed by the red box is the thinned sample for cross section view examination. (c) Centered dark-field TEM image and the corresponding selected area diffraction pattern of the cross section view confirmed that the hemisphere-like structure is still amorphous. (d) Larger size CuZr beam (1.5 μm ×1.5 μm ×8 μm) exhibited less extent of the mass transportation. (e) Current evolution measured during the NED process.

Figure 4. Molecular dynamics simulation on the mass transportation mechanism during the shrinking process of a partly melted Mo nanobeam. (a) The nanobeam with its axial direction $[1\,\bar{1}1]$ is divided into three regions: left dark red region (fixed), middle bright red region (kept at ~441 K) and right observation region (instantaneously heated up to ~ 4800 K). The latter are divided into ten small regions, marked with $R_{i,}$ i=1 to 10, from right free end to the left. (b) Morphology evolution of Mo nanobeam under surface tension. A mushroom shape is formed at 84 ps. Note that here we ignore the thermal conduction to external surroundings. (c) The mean square displacements of centers of mass (δ_{CM}) of different marked regions versus time. (d) The mean square displacement of individual atoms (δ_{atom}) versus time. The fact that $\delta_{CM} >> \delta_{atom}$ indicates that convection dominates shrinkage rather than self-diffusion of atoms.

Figure 5. Application of NED for ultrafast mass transportation and welding of small volume materials. (a) A piece of refractory Mo single crystal adhered on a W tip is driven to approach the Mo base material. (b) After the NED process, the two parts were weld together. (c) The beam fractured at the right end when the W tip is pulled back, which indicates the welding volume is mechanically strong. (d) Three separated CuZr glass beams are fabricated for three-end welding. (e) NED between the W tip and beam 1 resulted the welding of the 3 beams. (f) The cross section view of the welding zone.

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